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Biochar impact on Midwestern Mollisols and maize nutrient availability

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ABSTRACT

Biochar applications have been shown to increase crop yields on acidic and low activity soils in the tropics but fewer positive yield responses have been reported for temperate soils. We hypothesized that even without a yield response, applying biochar to a Midwestern Mollisol could improve soil quality and plant nutrient availability because of the carbon it supplies and its conditioning effect. Eighteen small field plots (23.7 m^2) on a glacial-till derived soil were established by incorporating 0 to 96 Mg ha^{-1} of hardwood biochar to a depth of 30 cm. Several soil quality indicators, plant nutrient availability, uptake, and yield of two consecutive maize (*Zea mays* L.) crops were monitored. Biochar application significantly increased soil pH, readily available water (RAW) content (defined as volumetric water available between −10 kPa and −100 kPa) and soil organic C (SOC). It decreased bulk density (BD), but had no consistent effect on soil infiltration rates, CEC, or nutrient uptake. Biochar application did increase grain yield during the first year by 11 to 55% following very high stover application rates (3.5× the typical amount), presumably because biochar mitigated adverse effects of allelochemicals released from the decomposing maize residue. There was no detectable biochar effect on maize yield during the second year when the crop was limited by severe drought.

1. Introduction

Biochar is increasingly being discussed as a potential amendment to sequester carbon and improve soil quality. Biochar amendments to agricultural soils have been shown to reduce nutrient leaching and to have positive effects on soil physical, chemical and microbiological properties (Lehmann et al., 2003; Liang et al., 2006; Laird et al., 2010a, b; Basso et al., 2013; Parvage et al., 2013), that may act in synergy and result in improved crop performance. However, soil responses to biochar applications are strongly influenced by the material's specific chemical and physical characteristics as well as the site-specific soil–biochar interactions. Therefore, predicting the exact effect of particular biochar on soil physicochemical properties and crop yield can pose a challenge (Biederman and Harpole, 2013).

The degree of uncertainty associated with characterizing biochars' behavior in soils also relates to differences in environment and soil type under which trials have been carried out. Generally, favorable effects of biochar applications on soil quality and crop productivity have been observed on highly weathered, nutrient-poor tropical soils. In these studies, biochar had positive effect on both, soil characteristics and crop performance, that were partly attributed to reduced Al toxicity in the rhizosphere (Glaser et al., 2002). These findings might not be relevant to other climatic regions or soils where Al toxicity is not an issue (Atkinson et al., 2010; Glaser et al., 2002; Lehmann, 2007; Lehmann et al., 2006). Limited field studies indicated that biochar addition to temperate region soils causes small and transient changes in agroecosystems where native soil fertility is sufficiently high (Jones et al., 2012). Thus application of biochar to soils of temperate regions may have no or limited effect on crop yields, unless biochar can ameliorate specific soil related productivity constrains (Guerena et al., 2013; Karer et al., 2013).

Increased water holding capacity and availability to plants on medium and coarse textured soils during periods of moisture stress is one potential benefit of applying biochar to temperate soils. Numerous reports indicate a positive soil water effect of biochar because of its high porosity and surface area. Glaser et al. (2002) demonstrated an 18% increase in biochar-amended soils relative to adjacent soils, while Basso et al. (2013) reported a 29 to 84% increase. A 10% increase in barley (*Hordeum sativum*) yield from a biochar amended Chernozem during a prolonged drought was attributed to increased plant available water (Karer et al., 2013).

High internal porosity of biochar creates a soil conditioning agent that can lower bulk density, affect pore size distribution, and potentially influence water percolation rates and nutrient leaching (Bell and Worrall, 2011). Similar to water sorption, capillary forces, along with electrostatic and complexation forces of biochar surfaces can also affect sorption capacity for organic and inorganic compounds. Biochar can

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thus have either positive or negative environmental and agronomic effects on fertilizers, pesticides and allelochemicals through adsorption (Kulmatiski and Beard, 2006; Laird et al., 2010a; Lehmann et al., 2003).

While controlled experiments under laboratory and greenhouse conditions provide valuable findings, relatively little research has been done to address the impact of biochar additions on soils of temperate regions under field production conditions. Our objective was to quantify effects of biochar application on selected soil physicochemical properties within a Midwestern USA Mollisol while monitoring nutrient availability, uptake and yield by maize over a two-year period.

2. Materials and methods

2.1. Biochar

Biochar was obtained from ICM, Inc. (Colwich, KS) who used a low-temperature auger bed gassifier operated between 500 and 575 °C to produce high carbon biochar from mixed hardwood [primarily oak (*Quercus* spp.), elm (*Ulmus* spp.) and hickory (*Carya* spp.)] woodchips. Particle size ranged from 0.1 mm to 2.0 cm with the majority of particles <1.0 mm. Volatiles, fixed C, ash, and moisture content were determined by proximate analysis using ASTM standard method D 1762-84 (2007), while total C, H, N, O, and S were determined by ultimate analysis (ASTM standard D3176-89, 2002). The biochar pH, (pH 8.8) was measured in DI water using a 1:50 solid to liquid ratio after 1 h of equilibration (Gaskin et al., 2008). Proximate and ultimate analytical results are given in Table 1. Overall, the biochar consisted of 78% C, 8% ash, and 13% volatile matter.

2.2. Experimental design

Field plots (23.7 m^2) were established on Clarion loam (fine-loamy, mixed, superactive, Mesic Typic Hapludolls) in October 2010 at the Iowa State University Boyd Research Farm in Boone County, Iowa. The field had been in a maize/soybean rotation from 2006 through 2008 and continuous maize since 2009.

Six biochar application rates, 0, 19.2, 38.3, 57.5, 76.6, and 95.8 Mg ha^{-1}, were replicated three times thus providing 18 field plots in the main experiment. Three additional plots, adjacent to the main experiment but not receiving biochar or rotary tillage were included as "standard management" controls for comparison. The experimental site is located on slightly to severely eroded Clarion soil with inherent soil quality, based on the relative degree of erosion, grading from the poorest (severely eroded) in the southwest corner to the best (slightly eroded) in the northeast corner. A 1.5 m buffer strip surrounded each plot to prevent potential confounding due to biochar movement by wind, water or tillage.

Biochar was surface applied in the fall of 2010 and immediately incorporated utilizing both rotary and moldboard plow tillage. This resulted in a relatively uniform distribution of biochar to a depth of approximately 30 cm and incorporated crop residue (6.5 Mg ha^{-1}) from the 2010 maize crop, but created a potentially erosive surface condition prior to the winter months. Therefore, an additional 22.6 Mg ha^{-1} of chopped maize residue was spread uniformly on the soil surface of the main experimental plots (but not the standard management plots) to minimize potential soil loss via erosion. In the spring of 2011, all plots were tilled with a tandem disk to incorporate the chopped residue before planting.

Table 1
Chemical properties of biochar determined by ultimate and proximate analysis. The results are reported on air-dry basis.

Proximate and ultimate analysis			
Constituent	g kg^{-1}	Constituent	g kg^{-1}
Moisture	7.4	H	17.6
Ash	76.6	N	6.4
Volatile	134.6	S	0.1
Fixed C	781.4	O	51.1

2.3. Fertilization practices

All plots received 44.8 kg ha^{-1} of P_2O_5 and 40.2 kg ha^{-1} of N as DAP and 67.2 kg ha^{-1} K as KCl after collecting initial soil samples but before biochar application in November 2010. During the 2011 growing season all plots received a total of 377 kg ha^{-1} of N as 32% UAN fertilizer in a split application. This high level of N fertilization was applied to mitigate the risk of N immobilization resulting from the high rate of maize residue applied the previous fall. After harvest in the fall of 2011, all plots and received 78.5 kg ha^{-1} of P_2O_5, 19.6 kg ha^{-1} S, 23.5 kg ha^{-1} N, 2.1 kg ha^{-1} Zn as MEZS, and 78.5 kg ha^{-1} of K as KCl. An additional 50 kg ha^{-1} of N as 32% UAN was applied at planting, and 180 kg ha^{-1} N (UAN) was applied using a split application on May 30 and June 8, 2012.

2.4. In-season measurements

Maize ('Pioneer Brand 36 V75') was planted on May 9, 2011 at a seeding rate of 79,074 seeds ha^{-1}. Resistance to penetration in the root zone (0 to 15 cm) as well volumetric soil moisture content (0 to 6 cm) was measured using a Penetrologger equipped with Theta moisture sensor (Eijkelkamp Inc., Giesbeek, The Netherlands) in mid-July. Ten measurements were collected and averaged across each plot. Plant tissue samples were taken after tasseling but prior to silking by collecting the leaf attached directly below the ear. Three leaf samples were taken from each of the four middle rows of each plot and dried at 50 °C to constant weight.

Maize ('Pioneer Brand P0461') was planted on April 27, 2012 at a seeding rate of 84,980 seeds ha^{-1}. During 2012 growing season surface volumetric moisture content was measured daily from June 21 to July 3 with a Theta moisture sensor. Infiltration and runoff rates were measured for a representative area in each plot using a sprinkle infiltrometer (Cornell University, Ithaca, NY).

2.5. Soil water retention and bulk density

Surface soil bulk density was determined on undisturbed soil cores collected in July 2012. Five samples were collected per plot using metal rings with an inner diameter of 7.5 cm and a height of 8.5 cm (Grossman and Reinsch, 2002). Soil water retention was determined on undisturbed surface soil samples collected after crop harvest in 2012. Three soil samples per plot were collected using metal rings (5 cm diameter by 3.8 cm height). Water retained at −10, −33, −100, and −500 kPa matric potential was determined by the pressure plate method (Dane and Hopmans, 2002) using a Pressure Plate Extractor (Soil Moisture Equipment Corp., Santa Barbara, CA, USA). The intact soil cylinders held in metal rings were initially saturated from the bottom up with 0.001 M $CaCl_2$ for 24 h at 20 °C, placed on a pressure plate, and pressure was incrementally increased to −10 and then −33 kPA. Water retained at −100 and −500 kPa was determined using soil placed in rubber rings (3 cm diameter by 1 cm height) and saturated from the bottom with 0.001 M $CaCl_2$ at 20 °C. Readily available water (RAW) content of each sample was determined by calculating the difference in volumetric water content held at −10 and −100 kPa (Fassman and Simcock, 2012).

2.6. Soil and plant analyses

One composite soil sample consisting of five cores (0–15 cm depth) was taken per plot in September of 2010 prior to biochar and synthetic fertilizer application (initial samples) and again on October 2012, two years after biochar application. Soil samples were analyzed for total C and N by high temperature combustion using a Carlo Erba NA1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ). Effective cation exchange capacity (ECEC) was determined using the method of Suarez (2008). Plant available nutrients were extracted using the Mehlich 3 method and analyzed by inductively coupled plasma-atomic emission spectroscopy (Mehlich, 1984). Soil pH was determined using the method described by Thomas (1996). Elemental composition of the plant tissue samples (P, K, Mg, Ca, S, B, Zn, Mn, Fe, Cu, Al, Na, and Mo) was determined by inductively coupled plasma-atomic emission spectroscopy following open vessel wet digestion with nitric acid (70%) and hydrogen peroxide (30%) on a Digibloc 3000 heating block at 95 °C for 90 min (AQAC Official Method 985.01; Isaac and Johnson, 1985). Fall stalk nitrate samples were analyzed using an extraction and cadmium reduction method described by Gelderman and Beegle (1998). This was done only in 2011 growing season as N deficiencies were suspected due to high amounts of maize stover applied the previous fall.

2.7. Crop harvest and yield measurements

Maize grain yields were estimated after plants reached physiological maturity in mid-October by hand-harvesting ears from 3.7 m of the middle four rows of each plot. Yields of above-ground biomass were estimated by harvesting stalks and dropped leaves from the center 1.0 m of the middle two rows of each plot, drying at 60 °C and then weighing. Above-ground biomass estimates reported in the manuscript include grain, stalks, leaves, and cobs.

2.8. Statistical analysis

The main experiment was set up as a pseudo Latin Square experimental design to account for some of the spatial variability in soil quality. Results from the external control plots are included to provide some estimate of the residue effects but are not included in the statistical analysis of the biochar effect. All statistical analyses were conducted using SAS 9.1 for Windows (SAS Institute). Statistical differences between biochar levels were determined using a generalized linear model (Proc GLM), $P \leq 0.05$. The relationships between variables were tested by regression procedure (Proc REG), $P \leq 0.05$.

3. Results

3.1. Soil chemical characteristics

Chemical properties of soil collected before and two years after biochar application are presented in Table 2. The initial sampling showed no significant differences among treatments, so we assume that the Pseudo Latin Square experimental design was effective at minimizing spatial variability effects of inherent soil quality. Based on Iowa State University soil test recommendations, P and K concentrations were in the deficient range (optimal range for Mehlich-3 P: 26–35 mg kg^{-1}; K: 111–170 mg kg^{-1}), so fertilizer supplying those nutrients was applied before the biochar application (see Materials and methods section).

Biochar had limited effect on soil chemical properties two years after application (Table 2). Significant differences were observed only for soil pH and total C content. Biochar increased soil pH by 1 to 1.4 units with the highest increase observed for the highest biochar rate; pH increased from 5.4 to 6.8 with 96 Mg biochar ha^{-1}. Total C increased from 15.3 g kg^{-1} on control plots to 23.4 g kg^{-1} on plots that received 96 Mg ha^{-1} biochar (Table 2). Based on proximate analysis (Table 1), application of biochar at the highest rate of 96 Mg ha^{-1} supplied about 75 Mg ha^{-1} of fixed C.

3.2. Soil physical characteristics

Application of biochar significantly ($P < 0.001$) increased volumetric water content in the surface 3 cm of soil both years (Figs. 1 and 2). When measured in July 2011, the average volumetric water content increased linearly ($r^2 = 0.80$) from 24.6% to 34.1% as the biochar application rate increased from 0 to 96 Mg ha^{-1} (Fig. 1). During the 2012 growing season, volumetric moisture content was monitored daily over 2-week period from June 21 to July 3 (Fig. 2). Soil moisture

Table 2
Initial (before biochar application) and final soil chemical characteristics.

	0	19	38	58	77	96
Samples collected in 2010 before biochar applications, Mg ha^{-1}						
P, mg kg^{-1}	21.8(7.7)	17.8(4.8)	22.7(10.3)	20.0(4.4)	18.9(4.4)	25.0(7.1)
K, mg kg^{-1}	104.5(24.5)	93.3(7.3)	92.7(9.0)	99.1(12.9)	97.7(11.0)	106.4(29.3*)
Na, mg kg^{-1}	12.1(5.3)	12.2(6.2)	12.0(13.0)	12.2(17.6)	12.2(20.3)	12.1(7.6)
Mg, mg kg^{-1}	228.7(20.1)*	243.9(7.1)*	229.0(11.9)*	239.5(27.8)*	224.9(19.1)*	227.2(23.5)*
Ca, mg kg^{-1}	2409.7(168)	2488.3(116)	2574.0(311)*	2462.3(64)	2259.0(26)	2552.3(124)*
Mn, mg kg^{-1}	98.7(17)*	106.3(7.5)*	114.4(25.2)*	106.0(11)*	98.3(23.2)*	104.2(15.3)*
Fe, mg kg^{-1}	197.8(30.7)*	214.5(31)*	194.2(39)*	209.1(33.2)*	198.1(48.7)*	210.2(19.6)*
Cu, mg kg^{-1}	1.48(0.15)	2.48(0.96)*	1.51(0.17)	1.59(0.08)	1.47(0.26)	1.63(0.24)*
Zn, mg kg^{-1}	0.20(0.07)	0.16(0.08)	0.13(0.07)	0.17(0.07)	0.20(0.16)	0.17(0.10)*
Soil pH	6.8(0.1)*	7.0(0.4)	7.0(0.5)	6.9(0.0)	6.9(0.5)	6.9(0.2)
ECEC, cmol kg^{-1}	12.4.(0.9)	12.7(0.9)	14.5(2.5)	12.9(0.7)	11.8(0.6)	12.9(1.1)
Total C, %	1.34(0.25)	1.35(0.22)	1.43(0.13)	1.34(0.10)	1.31(0.21)	1.38(0.17)
Samples collected in 2012 two years after biochar applications, mg kg^{-1}						
P, mg kg^{-1}	20.3(18.3)	9.0(2.6)	11.0(6.0)	21.9(10.6)	12.7(1.5)	20.0(4.0)
K, mg kg^{-1}	134.1(32.1)	150.6(48.7)	205.6(110.3)	152.6(14.3)	153.6(12.2)	208.8(76.4)*
Na, mg kg^{-1}	12.5(2.5)	18.6(3.0)	17.9(4.2)	17.6(2.7)	20.7(4.7)	24.7(6.9)
Mg, mg kg^{-1}	272.7(39.2)*	288.6(15.7)*	266.4(31.0)*	275.1(29.7)*	271.8(13.9)*	280.4(52.2)*
Ca, mg kg^{-1}	2734(241)	2993(98)	3473(1231)*	2934(241)	3079(109)	3434(276)*
Mn, mg kg^{-1}	73.4(8.8)*	75.9(22.0)*	79.6(27.3)*	73.6(23.7)*	70.6(25.0)*	69.3(5.9)*
Fe, mg kg^{-1}	129.0(21.8)*	134.9(45.5)*	109.4(21.5)*	132.0(24.6)*	105.3(19.4)*	115.9(23.8)*
Cu, mg kg^{-1}	2.7(1.5)	4.9(3.7)*	2.8(0.5)	4.1(1.6)*	3.5(0.8)	5.6(2.7)*
Zn, mg kg^{-1}	2.4(1.6)	3.6(2.2)	2.1(0.7)	5.5(5.4)	2.1(0.6)	4.3(1.6)*
Soil pH	5.4(0.5)b*	6.4(0.7)ab	6.4(0.9)ab	6.7(0.8)a	6.6(0.2)a	6.8(0.2)a
ECEC, cmol kg^{-1}	10.3(1.1)	12.4(6.3)	12.6(3.5)	10.2(2.4)	11.2(5.7)	12.6(5.6)
Total C, %	1.53(0.08)ab	1.46(0.3)b	2.03(0.34)ab*	1.93(0.27)ab*	2.07(0.22)ab*	2.34(0.51)a*

Values represented in table are means of three replications for 0–15 cm composite soil samples. Numbers in parenthesis represent standard deviations. Numbers followed by different letters indicate significant differences between treatments within a year. Numbers followed by the stars indicate significant differences between years.

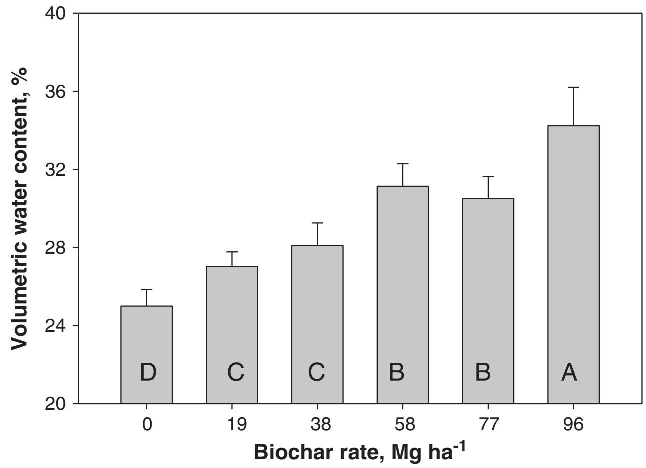

Fig. 1. Differences in volumetric water content (surface 0–3 cm soil) as affected by biochar applications. One time measurement was made in July, 2011.

content was consistently higher in biochar amended plots and the difference between control plots and those that received biochar was consistent throughout the monitoring period. On average, biochar application increased volumetric soil water content in the 0–3 cm layer by 12 to 44% for the 19 and 96 Mg ha^{-1} biochar application rate, respectively.

Soil penetration resistance and bulk density, indicators of soil compaction, were measured in 2011 and 2012, respectively. Average penetration resistance for the 0–15 cm depth ranged from 1.30 to 1.44 MPa for all biochar amended plots, which was not significantly different from the control plot average of 1.33 MPa. Bulk density measurements, however, showed significant impact of biochar application on soil compaction (Fig. 3). On average, biochar application decreased bulk density from about 1.65 g cm^{-3} on control plots to 1.50 g cm^{-3} on plots amended with 96 Mg biochar ha^{-1}. Biochar explained 61% of variability in bulk density values (Fig. 3). Despite a linear decrease in soil bulk density with increasing biochar application, there was no consistent

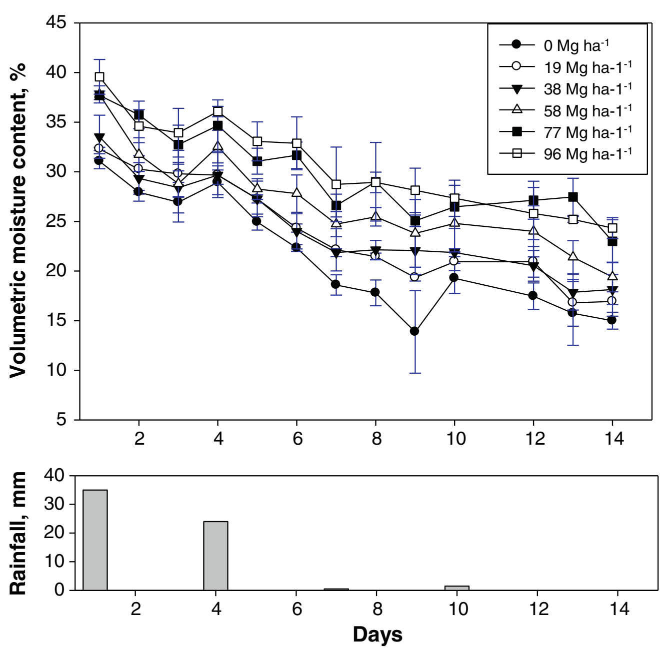

Fig. 2. Temporal variability of volumetric water content in the 0–3 cm surface soil layer as affected by biochar application rate. Moisture measurements were taken daily (with the exception of day 11) for the period starting June 21 and ending July 3, 2012.

effect on infiltration or surface runoff rates. Only plots that received 58 Mg ha^{-1} of biochar had significantly higher infiltration rates and lower runoff rates than the control plots (Fig. 4).

Water retention characteristics measured on samples collected two years post biochar application (Fall 2012) are shown in Fig. 5. No difference in the volume of water retained at saturation point was observed between treatments. Volumetric water content ranged from 0.50 cm^3 water per cm^3 soil for plots amended with 19 Mg ha^{-1} biochar to 0.51 cm^3 water per cm^3 soil for plots amended with 96 Mg ha^{-1} biochar and was not different from control plots (0.51 cm^3 cm^{-3}). Water transport and retention, however, is more affected by the relative abundance of macro- and micropores in a representative volume rather than the total pore volume. At matric tension of −10 kPa more water was retained by soil amended with 58 (11% increase, $P < 0.1$), 77 (14% increase, $P < 0.05$), and 96 (16% increase, $P < 0.05$) Mg ha^{-1} biochar compared to no-biochar control soils. At matric potential of −33 kPa more water was retained by soil amended with 96 Mg ha^{-1} biochar compared to control (14% increase). No significant difference in volumetric water content between biochar treatments was observed at matric potential of −100 kPa. Biochar amended soil had significantly greater RAW (water retained between −10 and −100 kPa tension) than no-biochar control soils (Fig. 6). Values of RAW for each treatment were 0.04, 0.07, 0.05, 0.09, 0.08 and 0.1 cm^3 of water per cm^3 of soil for the control, 19, 38, 58, 77 and 96 Mg ha^{-1}, respectively. Biochar application explained 35% of variability in RAW content ($P = 0.04$, data not shown).

3.3. Plant tissue analyses

In 2011, biochar applications did not have a significant effect on plant tissue N, K, S, B, Mg, Cu, or Zn concentrations, but P, Ca, Mn and Fe concentrations were all significantly lower in plants from plots receiving biochar than from the control plots (Table 3). Biochar application rate explained 22% ($P = 0.05$) and 43% ($P < 0.01$) of variability in Ca and Mn concentrations, respectively (data not shown). Despite the reductions in plant tissue P, Ca, Mn, and Fe concentrations with increasing biochar application rates, all plant nutrient levels (Table 3) were within the sufficiency range for plant growth (Vitosh et al., 1995).

End-of-season corn stalk nitrate test showed no N deficiencies among treatments; the nitrate concentrations for individual plots varied from 726 to 4480 mg kg^{-1} but all were within the optimal (700–2000 mg kg^{-1}) or excessive (>2000 mg kg^{-1}) range. In particular, corn stalk nitrate concentrations receiving 19, 77, and 96 Mg ha^{-1} biochar had significantly lower end-of-season concentrations of nitrate than stalks harvested from the control plots.

The 2010 biochar applications had no significant effect on the 2012 plant tissue Ca, B, Zn, or Fe concentrations (Table 3). However, Mg, S, Mn, and Cu concentrations were all significantly lower in plants from biochar treated plots when compared to the control plots. A significant negative relationship was observed between biochar application rate and Mg concentrations in maize tissue. Biochar application accounted for 51% ($P < 0.01$) of the variability in tissue Mg, however the mechanisms influencing Mg mobility and plant uptake are not clear.

Potassium uptake was significantly enhanced by biochar application with the greatest concentrations observed in plants from plots receiving 96 Mg ha^{-1} biochar (Table 3). A significant positive relationship between tissue K and biochar rate of application explained 24% ($P = 0.04$) of variability in plant K concentrations.

There was no clear relationship between biochar application rate and plant uptake of P, as plant tissue P concentrations were 4 to 8% lower for the 38 and 77 Mg ha^{-1} biochar treatments and 12% greater for the 96 Mg ha^{-1} biochar treatments (Table 3). Inconsistencies in plant uptake of P can be partly attributed to adsorption of both orthophosphate and organic P compounds on the biochar surfaces or through

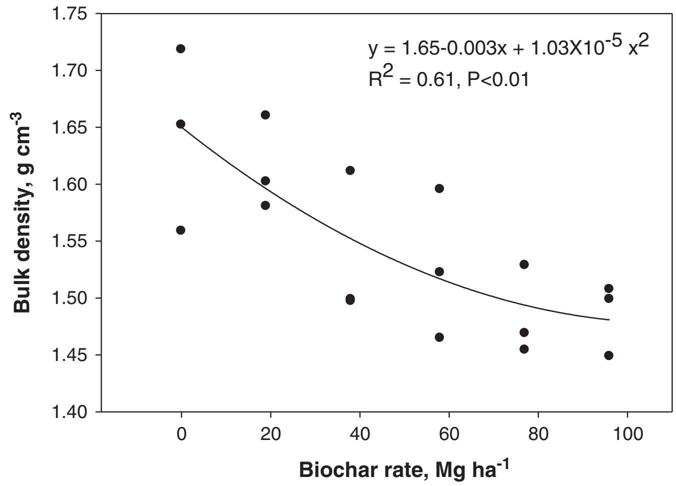

Fig. 3. Soil bulk density as affected by biochar application. Bulk density was measured in July 2012.

binding to positively charged metal complexes formed on biochar surfaces (Laird et al., 2010a; Parvage et al., 2013).

3.4. Biomass and grain yields

In 2011, biochar applications increased both grain and above-ground biomass yields (Fig. 7A). The greatest increase was observed for the first three increments of biochar application, where grain yield rose from 6.9 Mg ha^{-1} on control plots to 7.6, 8.1 and 10.2 Mg ha^{-1} on plots amended with 19, 38, and 58 Mg biochar ha^{-1}, respectively. Addition of biochar at rates of 77 and 96 Mg ha^{-1} did not further increase yield. A quadratic response model describing biochar rate and corn grain yield explained 52% of variability. Biomass yield increased from an average of 5 Mg ha^{-1} on control plots to 6.2 Mg ha^{-1} on plots receiving 96 Mg ha^{-1} of biochar. A linear model describing this relationship indicated that biochar explained 24% of variability (Fig. 7A).

In 2012, no clear trend in maize grain yield was observed, although plots amended with 38 Mg ha^{-1} biochar in 2010 produced significantly greater yield ($P = 0.06$) than those amended with 96 Mg ha^{-1} biochar (Fig. 7B). Biochar application did not affect above-ground biomass yields in 2012.

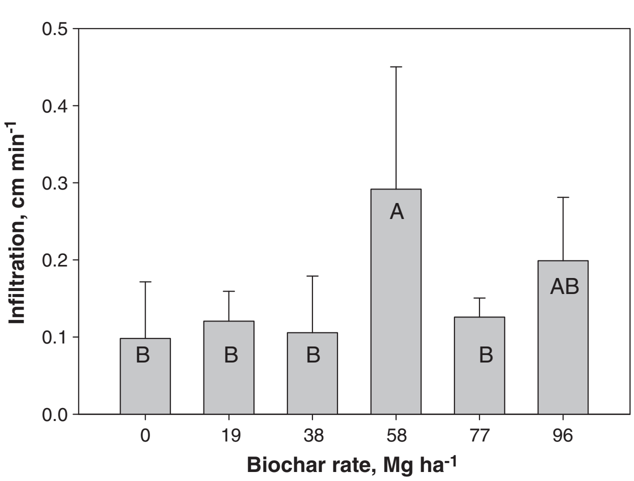

Fig. 4. Impact of biochar on infiltration rate of saturated soil two years after biochar application. Measured in July 2012. Bars that contain the same letters are not statistically different.

4. Discussion

4.1. Soil physical properties

Soil moisture responses measured in this study were consistent with previous laboratory and field studies (Karer et al., 2013; Karhu et al., 2011; Laird et al., 2010b) and suggest that biochar may help increase crop yields during periods of moisture stress. Biochar also reduced soil bulk density which generally implies increased pore volume. Decreases in bulk density with biochar application may be partly attributed to a dilution effect caused by adding light-weight, low density material to a more compacted mineral soil. Depending on the type of feedstock and pyrolytic conditions, particle density of biochars has been reported to range from 1.54 to 2.06 g cm^{-3} (Brewer et al., 2009) and could partly explain the observed decreased soil bulk density of biochar amended plots in our study.

4.2. Tissue analyses

There are several possible explanations for the observed biochar effects on plant nutrient concentrations. First, biochar was effective at increasing soil pH. Solubility and hence bioavailability of P, Mn, Cu and Fe decrease with increasing pH (Alam et al., 1999). Second, the negative relationships between biochar application rate and plant tissue nutrient concentrations could be partially explained by a "dilution effect",

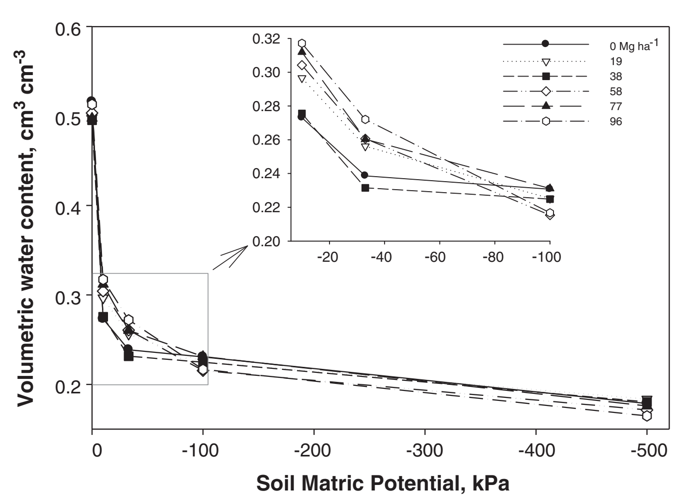

Fig. 5. Water retention curves for soils treated with different rates of biochar.

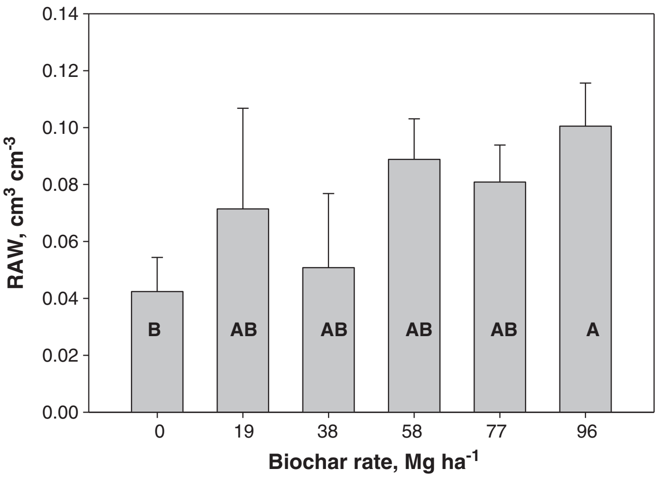

Fig. 6. Differences in readily available water (RAW) content as affected by biochar application rates. Bars that contain the same letters are not statistically different.

wherein rapid plant growth can cause a small decrease in nutrient concentration (Jarrell and Beverly, 1981). Biochar application positively affected above-ground biomass production in 2011, therefore some variation in plant tissue nutrient concentrations may be due to differences in dry matter production. Third, biochar applications are known to increase nutrient retention through cation and anion exchange and adsorption of dissolved organic matter which contains nutrients in organic form (Laird et al., 2010a; Liang et al., 2006). It is possible that some of the observed decreases in plant tissue nutrient concentrations were due to increased nutrient retention by the biochar in the soil. However, it is not possible to distinguish which of these processes were responsible for observed decreases in plant tissue P, Ca, Mn, and Fe concentrations with increasing biochar application rates.

Observed increase in plant K uptake in 2012, a drought year, can be explained by increased moisture content of biochar amended plots. Forms, availability and movement of K in the soil are strongly influenced by soil moisture regime (Chen and Fang, 2004; Zeng and Brown, 2000) with K deficiencies being commonly observed in dry years despite sufficient soil K levels (Ge et al., 2012). In our study, we observed significant positive relationship between plant uptake of K and average volumetric moisture content of surface 0–3 cm soil ($R^2 = 0.42$, $P = 0.04$). No relationship was observed between concentrations of K in the soil and uptake of K by plants, nor was there a relationship between plant K uptake and biochar application in either 2011 (a year with normal precipitation) or 2012 when crop growth was limited by a severe drought. Decreased tissue Mn and Cu concentrations can be explained by lower solubility and reduced plant availability due to an increase in pH following biochar application.

4.3. Grain and biomass yield

Biochar application resulted in significant increase in yields of grain and aboveground biomass in the first year after application, but no clear effect was observed the second year. Biochar itself can be a source of nutrients and can act as slow release fertilizer (Chan and Xu, 2009), but based on midseason plant tissue tests, this effect was not a likely explanation for yield variation as nutrient levels in all plant tissues tested were sufficient (Table 3).

Increased grain and biomass yield on biochar amended plots (Fig. 7A) could be partly attributed to significantly greater plant water supply during the 2011 growing season. Total growing season (April through August) precipitation that year was 55.4 cm, which is within one standard deviation of the 25-year average [60.2 ± 18.7 cm (Iowa Environmental Mesonet, 2012)] for this location. Although we cannot rule out differences in moisture supply as a factor affecting maize and biomass yield, there were no obvious signs of moisture stress and crop yields on external control plots and in adjacent fields were generally high.

Decomposition of large amounts of high C/N ratio maize residue (about 3.5 times the normal amount in this study) increases the risk of N deficiency due to N immobilization. To mitigate that risk, the total amount of N fertilizer applied for the 2011 crop exceeded the recommended rate by 75%. Furthermore, the end-of-season stalk nitrate test showed optimal to excessive nitrate concentrations for all samples. Therefore, we infer that N deficiency did not limit grain or biomass yield in 2011.

Table 3
Plant analyses in samples collected at silking in 2011 and 2012.

	Biochar rate, Mg ha^{-1}						
	0	19	38	58	77	96	Sufficiency range[a]
2011							
N, g kg^{-1}	35.6a	34.3a	34.0a	36.8a	34.4a	34.7a	29.0–35.0
P, g kg^{-1}	4.4a	4.0ab	3.6b	4.0ab	3.6b	3.7ab	3.0–5.0
K, g kg^{-1}	23.6a	22.2a	22.5a	22.5a	23.7a	23.5a	19.0–25.0
Mg, g kg^{-1}	2.8a	2.8a	2.3a	2.6a	2.5a	2.4a	1.6–6.0
Ca, g kg^{-1}	6.7a	6.8a	6.2ab	6.7a	5.9b	6.0ab	2.1–10.0
S, g kg^{-1}	1.9a	2.0a	2.0a	2.1a	1.9a	2.0a	1.6–5.0
B, mg kg^{-1}	5.00a	4.67a	4.00a	4.67a	4.00a	4.67a	4–25
Zn, mg kg^{-1}	23.7a	21.7a	19. 7a	21.3a	21.3a	20.7a	20–70
Mn, mg kg^{-1}	116a	99.7ab	82ab	88.3ab	67.7b	69.0b	20–150
Fe, mg kg^{-1}	187a	154. ab	145ab	164ab	139 b	147ab	21–250
Cu, mg kg^{-1}	9.67a	9.33a	8.67a	10.0a	9.0a	9.33a	6–20
2012							
P, g kg^{-1}	5.0b	5.2ab	4.8bc	5.2ab	4.6c	5.6a	3.0–5.0
K, g kg^{-1}	15.0c	14.5c	15.9bc	18.0ab	16.0bc	19.0a	19.0–25.0
Mg, g kg^{-1}	3.7a	3.6a	3.1ab	3.2ab	2.6b	2.9b	1.6–6.0
Ca, g kg^{-1}	4.8a	4.8a	4.7a	4.5a	4.0a	4.5a	2.1–10.0
S, g kg^{-1}	1.8a	1.8a	1.8a	1.8ab	1.6b	1.9a	1.6–5.0
B, mg kg^{-1}	7.5a	6.6a	6.3a	6.4a	5.9a	6.8a	4–25
Zn, mg kg^{-1}	61.1a	75.1a	74.1a	47.6a	95.3a	104.2a	20–70
Mn, mg kg^{-1}	42.3a	37.7ab	35.2ab	35.4ab	31.4b	32.0b	20–150
Fe, mg kg^{-1}	131a	139a	127a	137a	109a	151a	21–250
Cu, mg kg^{-1}	9.67a	10.61a	8.97ab	9.49a	7.55b	9.05ab	6–20

[a] Nutrient sufficiency range for maize ear leaf sampled at initial silking. Based on Tri-State Fertilizer recommendations (Vitosh et al., 1995). Numbers followed by the same letters are not statistically different at the alpha=0.05 level.

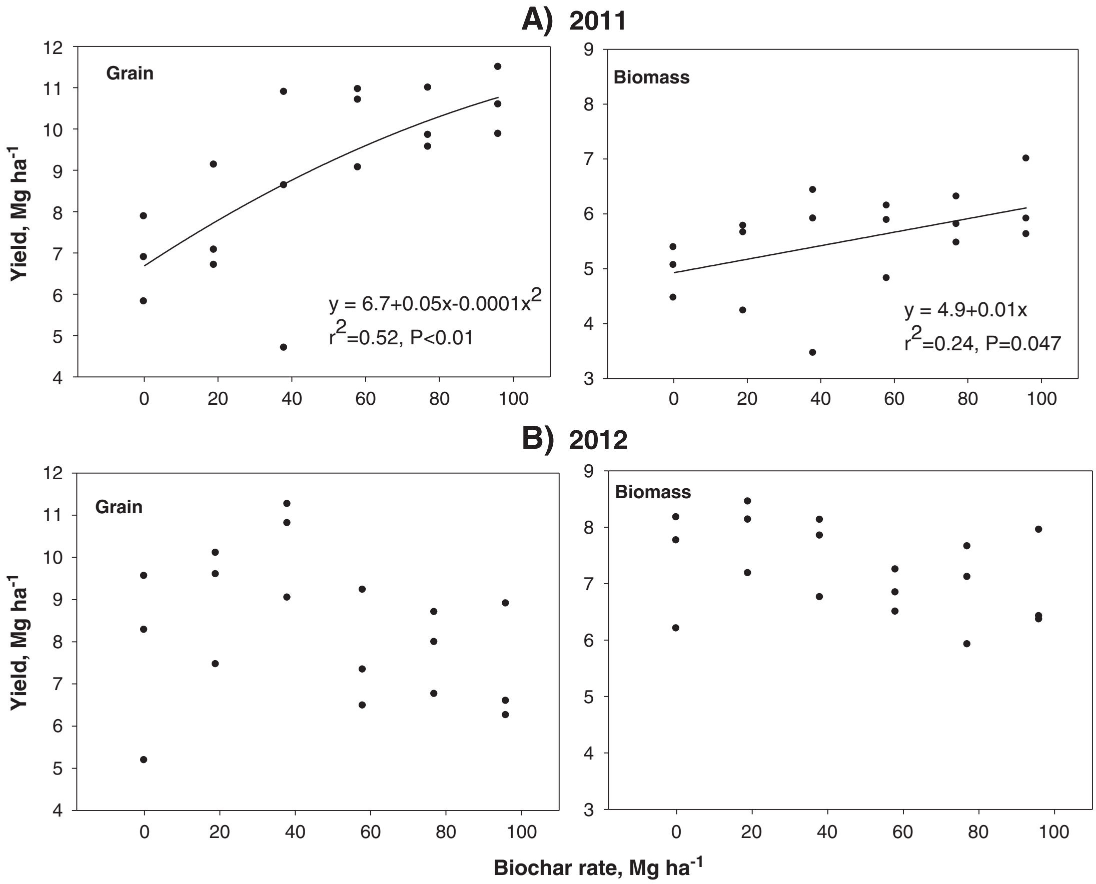

Fig. 7. Effect of biochar on grain yield and above-ground biomass in 2011 (A) and 2012 (B) growing seasons.

Crop residue decomposition can release phytotoxic compounds that can inhibit maize growth and development. We hypothesize that the 0.8 to 3.8 Mg ha^{-1} increase in grain yield on biochar amended plots can be attributed to adsorption and deactivation of potential phytotoxins on biochar surfaces. Although it is difficult to positively prove that phytotoxicity was responsible for decreased grain and biomass yield in the no-biochar control plots and those plots receiving low rates of biochar, the observed stress symptoms (i.e., stunted and chlorotic seedlings), which were first appeared shortly after germination and remained evident based on slow plant growth, development, and delayed silking, are all consistent with phytotoxicity (Rizvi et al., 1992; Rogovska et al., 2012). Furthermore, there was no reason to believe that moisture stress or nutrient deficiencies limited the 2011 crop. Thus we conclude that phytotoxicity was the most likely factor limiting yield in 2011 control plots and that biochar helped mitigate the phytotoxicity.

The potential for biochar to mitigate adverse effects of phytotoxicity is further supported by results of a germination study where biochar was shown to apparently adsorb and thereby suppress the negative effects of allelochemicals in aqueous extracts of maize stover (Rogovska et al., 2012) and by previous studies showing that activated carbon was similarly effective for mitigating allelopathy (Inderjit and Callaway, 2003; Kulmatiski and Beard, 2006).

By contrast with 2011, no excess residue was applied following the 2011 harvest and no significant relationship between biochar and grain or biomass yield was observed in 2012, despite a great deal of yield variability (5.1 to 11.3 Mg ha^{-1}). Yields on plots amended with 38 Mg ha^{-1} biochar were greater ($P = 0.06$) than those amended with 96 Mg ha^{-1} biochar, but no other significant differences were observed. Therefore, we suggest that factors other than allelopathy were responsible for yield variation in 2012. The most likely factor was a water deficit, since total growing season precipitation was only 41.6 cm, 30% below the 25-year average, and 13.8 cm less growing season precipitation than received in 2011. However, no significant relationship could be detected between average volumetric soil moisture content in the surface 6 cm or the RAW content (estimated from water retention curves) and grain yield (data not shown). We conclude that biochar amendments were not able to explain yield variability of the 2012 crop, despite evidence that biochar amendments increased total water and RAW in the surface soil. During a drought, such as 2012, plants draw water from the entire rooting volume not just the surface soil. It is likely that restrictive layers or other intrinsic properties limited the ability of the soil to supply moisture to the crop during the 2012 growing season.

5. Conclusions

Maize grain and biomass yields were increased by 11 to 55% in response to biochar amendments during the first year after biochar application on soils that also received 3.5× the normal amount of maize stover during the previous fall. For the second year of the study, only the normal amount of stover was left on the field and no significant effect of biochar on maize grain and biomass yields was observed. Sufficient nutrient levels in plant tissue tests and generally inverse correlations between plant nutrient uptake and grain and biomass yields indicated that nutrient availability was not limiting plant growth during the first year after biochar application. Biochar application significantly decreased soil bulk density and increased surface volumetric water content and RAW. However, there was adequate growing season precipitation during the first year of the study when crop yields responded to biochar applications and severe moisture stress due to drought conditions during the second year of the study when there was no crop yield response to the biochar applications. Furthermore, during the first year, stress symptoms, which occurred early in the growing season, were consistent with autotoxicity rather than moisture stress. Thus the preponderance of evidence suggests that during the first year of the study biochar mitigated adverse effects allelochemicals released from decomposing maize residue. We hypothesize that the allelochemicals were absorbed on biochar surfaces and thereby deactivated.

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